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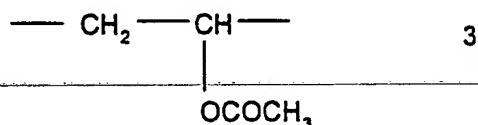
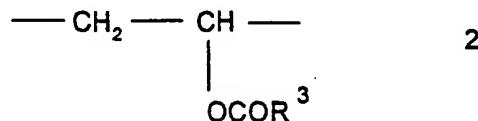
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(54) AGENTS POUR HUILES MINERALES AMELIORANT
L'ÉCOULEMENT

(54) FLOW IMPROVERS FOR MINERAL OILS



(57) Agent pour huiles minérales, améliorant l'écoulement. L'invention porte sur des mélanges renfermant A) un copolymère d'oléfines inférieures et d'esters vinyliques, comprenant a) 65-94 % en moles d'unités structurelles divalentes de formule 1 - CH₂ - CR¹R² - où R¹ et R² sont indépendamment l'un de l'autre un hydrogène ou un méthyle, b) 1-25 % en moles d'unités structurelles divalentes de formule 2 (voir formule 2 ci-haut), où R³ est un alkyle ramifié saturé C₆-C₁₆ contenant un atome de carbone tertiaire, et c) 5-35 % en moles d'unités structurelles divalentes de formule 3 (voir formule 3 ci-haut), où la somme des proportions molaires de comonomères de formules 2 et 3 se situe entre 6 et 35 % en moles, et au moins l'un des constituants B1) à B3) suivants : B1) un autre copolymère, tel que décrit en A); ou B2) un copolymère d'éthylène et d'ester vinylique renfermant de 5 à 35 % en moles d'unités structurelles dérivées de l'ester vinylique, en plus des unités structurelles dérivées de l'éthylène; ou B3) un terpolymère d'éthylène-ester vinylique-oléfine, où R³ est lié à la fonction carboxyle via son atome de carbone tertiaire.

(57) Flow improvers for mineral oils, the invention relates to mixtures comprising A) a copolymer of lower olefins and vinyl esters, comprising a) from 65 to 94 mol% of divalent structural units of the formula 1 - CH₂ - CR¹R² - in which R¹ and R², independently of one another, are hydrogen or methyl, b) from 1 to 25 mol% of divalent structural units of the formula 2 (see above formula 2) in which R³ is saturated, branched C₆-C₁₆-alkyl which contains a tertiary carbon atom, and c) from 5 to 35 mol% of divalent structural units of the formula 3 (see above formula 3) where the sum of the molar proportions of comonomers of the formulae 2 and 3 is between 6 and 35 mol%, and at least one of the following components B1) to B3): B1) a further copolymer as described under A), or B2) an ethylene-vinyl ester copolymer containing from 5 to 35 mol% of structural units derived from the vinyl ester, in addition to structural units derived fromethylene, or B3) an ethylene-vinyl ester-olefin terpolymer, wherein R³ is bonded to the carboxyl function via its tertiary carbon atom.



CA 02242474 1998-07-07

1997 DE 401

Abstract

Flow improvers for mineral oils

5 The invention relates to mixtures comprising

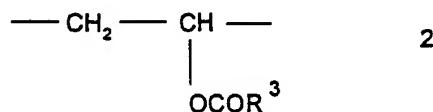
A) a copolymer of lower olefins and vinyl esters, comprising

a) from 65 to 94 mol% of divalent structural units of the formula 1



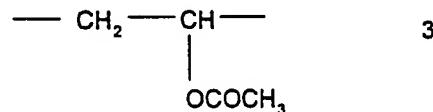
in which R¹ and R², independently of one another, are hydrogen or methyl,

15 b) from 1 to 25 mol% of divalent structural units of the formula 2



20 in which R³ is saturated, branched C₆-C₁₆-alkyl which contains a tertiary carbon atom, and

c) from 5 to 35 mol% of divalent structural units of the formula 3



where the sum of the molar proportions of comonomers of the formulae 2 and 3 is between 6 and 35 mol%,

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and at least one of the following components B1) to B3):

CA 02242474 1998-07-07

1997 DE 401

B1) a further copolymer as described under A), or

B2) an ethylene-vinyl ester copolymer containing from 5 to 35 mol% of structural units derived from the vinyl ester, in addition to structural units derived from
5 ethylene, or

B3) an ethylene-vinyl ester-olefin terpolymer,

wherein R³ is bonded to the carboxyl function via its tertiary carbon atom.

CA 02242474 1998-07-07

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1997 DE 401

Dr. KM/sch

Description

5 Flow improvers for mineral oils

The present invention relates to mixtures of copolymers of ethylene and vinyl esters of tertiary carboxylic acids, and their use as flow improvers for mineral oils.

10 Crude oils and middle distillates obtained by distillation of crude oils, such as gas oil, diesel oil or heating oil, contain, depending on the origin of the crude oils, various amounts of n-paraffins, which, when the temperature is reduced, crystallize out as platelet-shaped crystals and in some cases agglomerate with inclusion of oil. This causes an impairment of the flow properties of these oils or distillates, which can
15 result in problems during the recovery, transport, storage and/or use of the mineral oils and mineral oil distillates. In the case of mineral oils, this crystallization phenomenon can cause deposits on the walls of transportation pipelines, especially in winter, and in individual cases, for example during stoppage in a pipeline, can even cause complete blocking thereof. Precipitation of paraffins can also cause
20 problems during storage and further processing of the mineral oils. In winter, for example, it may in some circumstances be necessary to store the mineral oils in heated tanks. In the case of mineral oil distillates, the crystallization can result in blockage of the filters in diesel engines and furnaces, preventing reliable metering of the fuels and in some cases causing complete interruption of the supply of fuel or
25 heating medium.

In addition to the classical methods of eliminating the crystallized paraffins (thermal, mechanical or using solvents), which merely involve the removal of the precipitates which have already formed, recent years have seen the development of chemical
30 additives (so-called flow improvers or paraffin inhibitors), which, by interacting physically with the precipitating paraffin crystals, result in their shape, size and adhesion properties being modified. The additives act as additional crystal nuclei

CA 02242474 1998-07-07

2

and in some cases crystallize with the paraffins, resulting in an increased number of relatively small paraffin crystals having a modified crystal shape. Part of the action of the additives is also explained by dispersal of the paraffin crystals. The modified paraffin crystals have a lower tendency toward agglomeration, so that the oils to which these additives have been added can still be pumped and/or processed at temperatures which are frequently more than 20° lower than in the case of oils containing no additives.

The flow and low-temperature behavior of mineral oils and mineral oil distillates is described by indicating the pour point (determined in accordance with ISO 3016) and the cold filter plugging point (CFPP, determined in accordance with EN 116). Both parameters are measured in °C.

Typical flow improvers for crude oils and middle distillates are copolymers of ethylene with carboxylates of vinyl alcohol. Thus, DE-A-11 47 799 proposes adding oil-soluble copolymers of ethylene and vinyl acetate having a molecular weight of between about 1000 and 3000 to petroleum distillate fuels having a boiling point of between about 120 and 400°C. Preference is given to copolymers comprising from about 60 to 99% by weight of ethylene and from about 1 to 40 % by weight of vinyl acetate. They are particularly effective when prepared by free-radical polymerization in an inert solvent at temperatures of from about 70 to 130°C and pressures of from 35 to 2100 bar above atmospheric pressure(DE-A-19 14 756).

The prior art also describes mixtures of copolymers as flow improvers.

DE-A-22 06 719 discloses mixtures of ethylene-vinyl acetate copolymers having various comonomer contents for improving the low-temperature flow behavior of middle distillates.

DE-A-20 37 673 discloses synergistic mixtures of ethylene-vinyl ester copolymers of various molecular weight as flow improvers.

CA 02242474 1998-07-07

3

EP-A-0 254 284 discloses mixtures of ethylene-vinyl acetate copolymers with ethylene-vinyl acetate-diisobutylene terpolymers as flow improvers for mineral oils and mineral oil distillates.

5 EP-A-0 648 247 discloses mixtures of at least 2 different ethylene-vinyl acetate copolymers and their use as flow improvers for mineral oils, where the copolymers are firstly hydrolyzed and then re-esterified.

10 EP-A-0 648 257 discloses mixtures of at least 2 ethylene-vinyl ester copolymers in which the vinyl esters are derived from carboxylic acids having 2 to 7 carbon atoms.

15 EP-B-0 648 258 discloses ternary mixtures of ethylene-vinyl ester copolymers in which one of the mixture components contains between 7.5 and 35 mol% of the vinyl ester comonomer and another of the mixture components contains less than 10 mol% of the vinyl ester copolymers.

20 EP-A-0 113 581 discloses mixtures of two ethylene-vinyl ester copolymers in which the vinyl ester is derived from a carboxylic acid having 1 to 4 carbon atoms. One of the copolymers is a paraffin crystal nucleating agent, while the other copolymer is a growth inhibitor.

25 EP-A-0 741 181 discloses mixtures of two copolymers, at least one of which contains a vinyl ester containing alkyl or alkenyl radicals having more than 4 carbon atoms as comonomer.

The effectiveness of the known additives for improving the properties of mineral oil fractions depends, inter alia, on the origin of the mineral oil from which they have been obtained and thus, in particular, on its composition. Additives which are highly suitable for modifying certain properties of fractions of one crude oil may therefore give entirely unsatisfactory results in distillates obtained from crude oils of another origin.

CA 02242474 1998-07-07

4

Additives are now available which have a broad range of applications, i.e. significantly improve the low-temperature flow properties of mineral oils and mineral oil fractions having different origins. Nevertheless, there are cases in which they are less suitable or even unusable, for example because they contribute only little

5 toward increasing the flowability at low temperatures. The causes of this are many fold; the tapping of raw materials that have hitherto not been used, the different processing of the primary products and new market requirements may be mentioned as examples. A further disadvantage of many additives is that they impair the filterability of mineral oil distillates above the cloud point.

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In order to prevent the filtration problems, it is therefore necessary to observe special mixing conditions, such as high temperature of mineral oil and/or additive, particularly in the case of the ethylene-vinyl acetate copolymers. By contrast, terpolymers made from ethylene, vinyl acetate and vinyl esters of neocarboxylic acids (Versatic acids) are distinguished by very good solubility, but do not sufficiently lower the CFPP, in particular at relatively high comonomer contents. A further problem is storage of the additive concentrates. Owing to the limited solubility in organic solvents and the comparatively high density of the copolymers, sedimentation occurs in the storage container, in particular at low storage

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20 temperatures.

The object was therefore to find mineral oil and mineral oil distillate additives which both result in very good CFPP lowering and are sufficiently soluble, even at low temperatures, to prevent the filtration problems which occur in the case of the flow improvers of the prior art. In addition, improved sedimentation stability of the

25 concentrates (suspensions) should also be achieved, even at low temperatures.

Surprisingly, it has been found that this object can be achieved by mixtures which comprise a terpolymer of ethylene, vinyl acetate and a vinyl neocarboxylate and a copolymer of ethylene and vinyl acetate. The object is also achieved by mixtures of two of said terpolymers having different comonomer contents and/or molecular

CA 02242474 1998-07-07

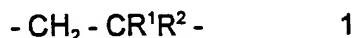
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weights, and one of said terpolymers and ethylene-vinyl acetate-olefin terpolymers.

The invention relates to mixtures comprising

5 A) a copolymer of lower olefins and vinyl esters, comprising

a) from 65 to 94 mol% of divalent structural units of the formula 1

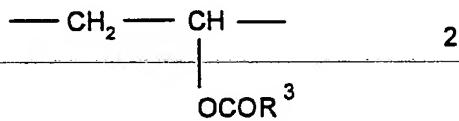


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in which R¹ and R², independently of one another, are hydrogen or methyl,

b) from 1 to 25 mol% of divalent structural units of the formula 2

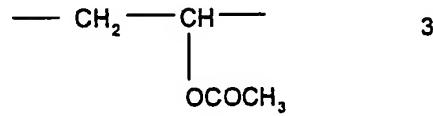
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in which R³ is saturated, branched C₆-C₁₆-alkyl which contains a tertiary carbon atom, and

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c) from 5 to 35 mol% of divalent structural units of the formula 3



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where the sum of the molar proportions of comonomers of the formulae 2 and 3 is between 6 and 35 mol%,

and at least one of the following components B1) to B3):

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B1) a further copolymer as described under A), or

CA 02242474 1998-07-07

6

- B2) an ethylene-vinyl ester copolymer containing from 5 to 35 mol% of structural units derived from the vinyl ester, in addition to structural units derived from ethylene, or
- 5 B3) an ethylene-vinyl ester-olefin terpolymer,

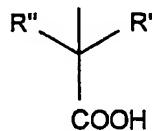
wherein R³ is bonded to the carboxyl function via its tertiary carbon atom.

Preferred vinyl esters for component B2) are vinyl acetate and vinyl propionate.
 10 Preferred vinyl esters for component B3) are vinyl acetate, vinyl propionate, vinyl hexanoate, vinyl laurate and vinyl esters of neocarboxylic acids, here in particular of neononanoic, neodecanoic and neoundecanoic acids. Preferred olefins are vinyl ethers, alkyl acrylates, alkyl methacrylates, isobutylene or higher olefins having at least 5 carbon atoms, preferred higher olefins being hexene, 4-methylpentene,
 15 octene and diisobutylene.

The mixing ratio between components A) and B) is preferably from 20:1 to 1:20, in particular from 10:1 to 1:10 by weight.

20 R¹ and R² are preferably hydrogen. R³ is preferably a neoalkyl radical having 7 to 11 carbon atoms, in particular a neoalkyl radical having 8, 9 or 10 carbon atoms. The neoalkanoic acids from which the abovementioned neoalkyl radicals can be derived are described by the formula 4:

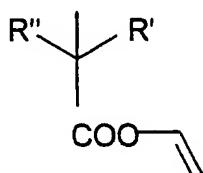
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30 R' and R'' are linear alkyl radicals, together preferably having 5 to 9, in particular 6 to 8, especially 7 or 8, carbon atoms. Accordingly, the vinyl ester used for the copolymerization has the formula 5:

CA 02242474 1998-07-07

7



- 5 Preference is given to the vinyl esters of neononanoic, neodecanoic and neoundecanoic acid. Copolymer A) preferably contains from 1 to 15 mol% of the structural units of the formula 2.
The sum of the molar proportions of comonomers of the formulae 2 and 3 is preferably between 6 and 20 mol%.

- 10 The copolymers used for the novel mixtures can be prepared by conventional copolymerization processes, for example suspension polymerization, solution polymerization, gas-phase polymerization or high-pressure bulk polymerization.
Preference is given to high-pressure bulk polymerization, preferably at pressures of
- 15 from 50 to 400 MPa, in particular from 100 to 300 MPa, and preferably at temperatures of from 50 to 300°C, in particular from 100 to 250°C. The reaction of the monomers is initiated by initiators which form free radicals (free-radical chained initiators). This class of substances includes, for example, oxygen, hydroperoxides, peroxides and azo compounds, such as cumene hydroperoxide, t-butyl
- 20 hydroperoxide, dilauryl peroxide, dibenzoyl peroxide, bis(2-ethylhexyl) peroxide carbonate, t-butyl perpivalate, t-butyl permaleate, t-butyl perbenzoate, dicumyl peroxide, t-butyl cumyl peroxide, di(t-butyl) peroxide, 2,2'-azobis(2-methylpropionitrile) and 2,2'-azobis(2-methylbutyronitrile). The initiators are employed individually or as a mixture of two or more substances in amounts of from
- 25 0.001 to 20% by weight, preferably 0.01 to 10% by weight, based on the monomer mixture.

- The novel mixtures preferably have melt viscosities at 140°C of from 20 to 10,000 mPas, in particular from 30 to 5000 mPas, especially from 50 to 2000 mPas.
30 The desired melt viscosity of the mixtures is established by varying the mixing ratio of the copolymers.

CA 02242474 1998-07-07

8

The copolymers mentioned under A), B1), B2) and B3) can contain up to 5 mol%, preferably up to 2 mol%, of further comonomers. Examples of such comonomers are vinyl esters, vinyl ethers, alkyl acrylates, alkyl methacrylates having C₁- to C₂₀-alkyl radicals, isobutylene or higher olefins having at least 5 carbon atoms. Preferred higher olefins are hexene, 4-methylpentene, octene and diisobutylene.

The high-pressure bulk polymerization is carried out batchwise or continuously in known high-pressure reactors, for example autoclaves or tubular reactors, the latter having proved particularly successful. Solvents, such as aliphatic and/or aromatic hydrocarbons or hydrocarbon mixtures, benzene or toluene, may be present in the reaction mixture. The polymerization is preferably carried out in the absence of a solvent. In a preferred embodiment of the polymerization, the mixture of the monomers, the initiator and, if used, the moderator is fed to a tubular reactor via the reactor inlet and via one or more side branches. The monomer streams here can have different compositions (EP-A-0 271 738).

The novel mixtures are added to mineral oils or mineral oil distillates in the form of solutions or dispersions. These solutions or dispersions preferably comprise from 1 to 90% by weight, in particular from 5 to 80% by weight, of the novel mixtures. Suitable solvents or dispersion media are aliphatic and/or aromatic hydrocarbons or hydrocarbon mixtures, for example gasoline fractions, kerosine, decane, pentadecane, toluene, xylene, ethylbenzene or commercial solvent mixtures, such as Naphtha, [®]Shellsoll AB, [®]Solvesso 150, [®]Solvesso 200, [®]Exxsol, [®]ISOPAR and [®]Shellsol D products. The solvent mixtures mentioned contain various amounts of aliphatic and/or aromatic hydrocarbons. The aliphatics can be straight-chain (n-paraffins) or branched (iso-paraffins). Aromatic hydrocarbons can be monocyclic, bicyclic, or polycyclic and may contain one or more substituents. Mineral oils or mineral oil distillates whose rheological properties have been improved by the novel mixtures contain from 0.001 to 2% by weight, preferably from 0.005 to 0.5% by weight, of the mixtures, based on the distillate.

With the same result of optimizing the effectiveness as flow improvers for certain substrates, the novel mixtures can also be employed together with one or more oil-soluble coadditives which even alone improve the low-temperature flow properties of crude oils, lubricating oils or fuel oils. Examples of such coadditives are polar 5 compounds which effect paraffin dispersal (paraffin dispersants) and comb polymers.

Paraffin dispersants reduce the size of the paraffin crystals and have the effect that the paraffin particles do not deposit, but instead remain colloidally dispersed with a 10 significantly reduced tendency to sediment. Paraffin dispersants which have proven successful are oil-soluble polar compounds containing ionic or polar groups, for example amine salts and/or amides, which are obtained by reacting aliphatic or aromatic amines, preferably long-chain aliphatic amines, with aliphatic or aromatic mono-, di-, tri- or tetracarboxylic acids or anhydrides thereof (US-4,211,534). Other 15 paraffin dispersants are copolymers of maleic anhydride and α,β -unsaturated compounds, which can, if desired, be reacted with primary monoalkylamines and/or aliphatic alcohols (EP-A-0 154 177), the products of the reaction of alkenylspirobislactones and amines (EP-A-0 413 279) and, as described in EP-A-0 606 055, products of the reaction of terpolymers based on α,β -unsaturated 20 dicarboxylic anhydrides, α,β -unsaturated compounds and polyoxyalkenyl ethers of lower unsaturated alcohols. Alkylphenol-formaldehyde resins are also suitable as paraffin dispersants.

The term comb polymers is taken to mean polymers in which hydrocarbon radicals 25 having at least 8, in particular at least 10, carbon atoms are bonded to a polymer backbone. Preference is given to homopolymers whose alkyl side chains contain at least 8 and in particular at least 10 carbon atoms. In the case of copolymers, at least 20%, preferably at least 30%, of the monomers have side chains (c.f. Comb-like Polymers - Structure and Properties; N.A. Platé and V.P. Shibaev, J. Polym. Sci. 30 Macromolecular Revs. 1974, 8, 117 ff). Examples of suitable comb polymers are fumarate-vinyl acetate copolymers (c.f. EP-A-0 153 176), copolymers of a C₆-C₂₄- α -

CA 02242474 1998-07-07

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olefin and an N-C₆- to C₂₂-alkylmaleimide (c.f. EP-A-0 320 766), furthermore esterified olefin-maleic anhydride copolymers, polymers and copolymers of α-olefins and esterified copolymers of styrene and maleic anhydride.

- 5 The mixing ratio (in parts by weight) of the novel mixtures with paraffin dispersants or comb polymers is in each case from 1:10 to 20:1, preferably from 1:1 to 10:1.

The novel mixtures are suitable for improving the low-temperature flow properties of animal, vegetable or mineral oils. They are particularly suitable for use with middle 10 distillates. The term middle distillates is taken to mean, in particular, mineral oils which have been obtained by distillation of crude oil and boil in the range from 120 to 400°C, for example kerosine, jet fuel, diesel and heating oil. Advantages of the novel mixtures are their CFPP synergism compared with the individual components and good filterability above the cloud point of the oils containing additives, although 15 individual components are not filterable. The concentrates have a significantly improved shelf life at low temperatures.

The novel mixtures can be used alone or together with other additives, for example dewaxing auxiliaries, corrosion inhibitors, antioxidants, lubricity additives or sludge 20 inhibitors.

Examples

The following polymers were employed, in each case in the form of a 50% 25 suspension in kerosine (the abbreviations are as follows:

E = ethylene, VA = vinyl acetate, VeoVa = vinyl neodecanoate,

V₁₄₀ = melt viscosity at 140°C, measured in accordance with ISO 3219):

- A) E-VA copolymer containing 32% by weight of VA, V₁₄₀ = 125 mPas
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B) E-VA copolymer containing 28% by weight of VA, V₁₄₀ = 300 mPas

CA 02242474 1998-07-07

11

- C) E-VA-diisobutylene terpolymer containing 25% by weight of VA and 5% by weight of diisobutylene, $V_{140} = 280$ mPas
- 5 D) E-VA-VeoVa terpolymer containing 25% by weight of VA and 9.5% by weight of VeoVa, $V_{140} = 850$ mPas in accordance with EP 493769
- E) E-VA-VeoVa terpolymer containing 31% by weight of VA and 8% by weight of vinyl neodecanoate, $V_{140} = 110$ mPas in accordance with EP 493769
- 10 F) E-VA-VeoVa terpolymer containing 32% by weight of VA and 11% by weight of vinyl neodecanoate, $V_{140} = 260$ mPas in accordance with EP 493769
- G) E-VA-VeoVa terpolymer containing 31% by weight of VA and 9% by weight of vinyl neodecanoate, $V_{140} = 230$ mPas

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Table 1: Characterization of the test oils (data in °C)

	Test oil 1	Test oil 2	Test oil 3	Test oil 4	Test oil 5
Start of boiling	174	166	180	166	165
20 20% of boiling point	204	209	268	214	109
50% of boiling point	239	252	307	282	243
90% of boiling point	328	315	350	356	327
End of boiling	367	337	336	376	357
Cloud Point	-8	-12	0	+4.2	-7.2
25 CFPP	-10	-16	-3	+3	-9

Solubility of the polymer mixtures

The solubility of the polymers and their mixtures was determined in a filtration test as follows: 130 ml of test oil 1 were mixed at room temperature with, unless stated

CA 02242474 1998-07-07

12

otherwise, 500 ppm of the additive conditioned at 40°C. After the vessel had been swirled around 20 times, a visual check was made as to whether additive residues were visible, the mixture was then filtered through a 0.8 µm cellulose nitrate filter (diameter 25 mm) under a vacuum of 200 mbar. A filtration time of less than five minutes for the entire volume of oil indicates good solubility of the additive. For a filtration time of more than five minutes, the volume filtered in this time was noted. The additives indicated were employed as 50% dispersions in kerosine.

Table 2 : Solubility of the polymer mixtures (test oil 1)

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Pure copolymer	Filtration time	Volume
Blank value (= no additive)	36 sec	-
A)	-	90 ml
B)		Additive insoluble
C)		Additive insoluble
D)		Additive insoluble
E)	65 sec	-
F)	43 sec	-

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Mixtures

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A + E (1:1)	72 sec	-
D + F (8:1)	55 sec	-
A + F	58 sec	-
B + E (1:1)	52 sec	-
B + E (1:1), 1000 ppm	54 sec	-
C + E (1:4)	175 sec	-

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CA 02242474 1998-07-07

13

Solubility of the polymers and mixtures (test oil 5):

	Pure copolymers and mixtures	Filtration time	Volume
5	A)	300 sec	230 ml
	B)	Additive insoluble	-
	E)	32 sec	-
	G)	33 sec	-
	A + G (1:1)	73 sec	-
	B + E (1:3)	125 sec	-
	Blank value	31 sec	-

Sedimentation stability

In order to assess the sedimentation behavior of dilute suspensions of flow

15 improvers, 50% solutions of the copolymer waxes in kerosine were prepared at from
 80 to 100°C and diluted with a further 9 parts of kerosine (room temperature),
 forming suspensions which were cloudy at room temperature. Their sedimentation
 behavior was assessed over a period of two weeks from the amount of sediment. In
 order to quantify the sedimentation behavior, the WDI (wax dispersion index) was
 20 determined.

$$WDI = \frac{\text{volume of sediment}}{\text{total volume}} \cdot 100\%$$

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A high WDI indicates low sedimentation and thus good stability of the suspension.

CA 02242474 1998-07-07

14

Table 3

		Wax Dispersion Index (WDI, %)					
		Product	Appearance RT	3 Days	6 Days	10 Days	14 Days
5	A	sign. cloudy	92	92	2	3	
	D	sign. cloudy	95	20	2	1	
	E	clear	100	100	100	100	
	D + F	sign. cloudy	97	97	91	1	
	E + D + F	slightly cloudy	100	100	100	100	
	A + F	slightly cloudy	100	100	100	100	
	A + E	slightly cloudy	100	100	100	100	

CFPP Synergism

15 Tables 4 to 6 show the superior effectiveness of the novel polymer mixtures compared with the individual components as additives for mineral oils and mineral oil distillates with reference to the CFPP test (cold filter plugging test in accordance with EN 116). The additives are employed as 50% suspensions in kerosine. Data in °C.

20 Table 4: CFPP synergism in test oil 2

	400 ppm	600 ppm
A	-17	-21
E	-18	-22
A+E	-21	-24

CA 02242474 1998-07-07

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Table 5: CFPP synergism in test oil 3

	600 ppm	800 ppm	1000 ppm
A	-6	-11	-14
E	-6	-10	-14
F	-5	-8	-9
A+F	-7	-14	-16
E+F	-6	-13	-17

10 Table 6: CFPP synergism in test oil 4

	200 ppm	300 ppm	400 ppm
A	0	0	-1
B	0	-3	-4
E	+2	0	+1
G	+1	-2	-4
A + G (1:1)	-1	-6	-7
B + E (1:3)	-1	-5	-6

20 List of trade names used

Solvent Naphtha aromatic solvent mixtures having a boiling range of from

[®]Shellsol AB 180 to 210°C

[®]Solvesso 150

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^aSolvesso 200 aromatic solvent mixture having a boiling range of from 230 to 287°C

[®]Exxsol Dearomatized solvent in various boiling ranges, for example [®]Exxsol D60: 187 to 215°C

CA 02242474 1998-07-07

16

[®]ISOPAR (Exxon) isoparaffinic solvent mixture in various boiling ranges,
for example [®]ISOPAR L: 190 to 210°C

[®]Shellsol D mainly aliphatic solvent mixture in various boiling ranges.

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CA 02242474 1998-07-07

17

1997 DE 401

Claims

1. A mixture comprising

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A) a copolymer of lower olefins and vinyl esters, comprising

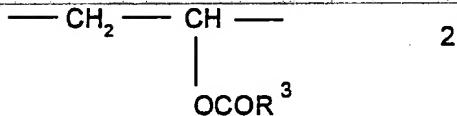
a) from 65 to 94 mol% of divalent structural units of the formula 1

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in which R¹ and R², independently of one another, are hydrogen or methyl,

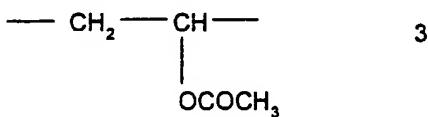
b) from 1 to 25 mol% of divalent structural units of the formula 2

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in which R³ is saturated, branched C₆-C₁₆-alkyl which contains a tertiary
20 carbon atom, and

c) from 5 to 35 mol% of divalent structural units of the formula 3

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where the sum of the molar proportions of comonomers of the formulae 2 and
3 is between 6 and 35 mol%,

30 and at least one of the following components B1) to B3):

CA 02242474 1998-07-07

18

1997 DE 401

- B1) a further copolymer as described under A), or
- B2) an ethylene-vinyl ester copolymer containing from 5 to 35 mol% of structural units derived from the vinyl ester, in addition to structural units derived from
5 ethylene, or
- B3) an ethylene-vinyl ester-olefin terpolymer,

wherein R³ is bonded to the carboxyl function via its tertiary carbon atom.

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2. A mixture as claimed in claim 1, wherein R¹ and R² are hydrogen.
3. A mixture as claimed in claim 1 and/or 2, wherein R³ is a neoalkyl radical having 7 to 11 carbon atoms, in particular a neoalkyl radical having 8, 9 or 10 carbon
15 atoms.
-
4. A mixture as claimed in one or more of claims 1 to 3, wherein copolymer A) contains from 1 to 15 mol% of structural units of the formula 2.
- 20 5. A mixture as claimed in one or more of claims 1 to 4, which has a melt viscosity at 140°C of from 20 to 10,000 mPas, in particular from 30 to 5000 mPas, especially from 50 to 2000 mPas.
- 25 6. A mixture as claimed in one or more of claims 1 to 5, wherein the copolymers mentioned under A), B1), B2) and B3) contain up to 5 mol% of further comonomers.
- 30 7. A mixture as claimed in claim 6, which contains, as further comonomers, vinyl esters, vinyl ethers, alkyl acrylates, alkyl methacrylates, isobutylene or higher olefins having at least 5 carbon atoms, preferably hexene, 4-methylpentene, octene or diisobutylene.

CA 02242474 1998-07-07

19

1997 DE 401

8. A mixture as claimed in one or more of claims 1 to 7, which contains paraffin dispersants and/or comb polymers.
9. A mixture as claimed in one or more of claims 1 to 8, which has an A:B mixing ratio of from 20:1 to 1:20, in particular from 10:1 to 1:10, by weight.
10. A method of using a mixture as claimed in one or more of claims 1 to 9 as an additive for improving the low-temperature flow properties of mineral oils.
- 10 11. An oil containing a mixture as claimed in one or more of claims 1 to 9.

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